Effect of Industrial By-products Fillers on the Properties of Blended Cements in Sulphate Environments

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Abstract

In previous studies, we have investigated the durability of normal concrete in various sulphates environments. The contribution of this study is the addition of industrial by-products fillers: granulated blast furnace slag and marble powder. These two fillers do not need any calorific energy compared to clinker manufacturing. From an environmental perspective, no more carbon dioxide is produce when these two materials are used. Furthermore, slag and powder marble are waste that should be stocked in adapted landfills.
Samples of normal mortar were exposed for 12 months to two sulphate environments: ammonium sulphate and sulphuric acid at two concentrations (0.05 and 0.25 mol/L). The evolution of crystalline phases is analyzed by XRD and minerals are observed by SEM, microanalysis (EDS linked to SEM) confirms their chemical composition. These determinations involve both the superficial formations that internal training due to conservation bath. For a low concentration of suphate (0.05 mol/L), the results show that the crystalline phases of cement (CSH, CH, ettringite) seem unaffected in the interior of the sample where the sulphur is completely absent. On the other hand, the ammonium sulphate penetrates deeper (4mm) to a high concentration (0.25 mol/L). However in the case of attack by sulphuric acid, samples develop a dense surface gypsum deposit. The mechanical strength, including bending strength to be known very sensitive to surface, is important to study this durability.

Keywords: *Durability, Ammonium sulphate, sulphuric acid, Slag, Marble.*

1 Introduction

The deterioration of concrete in sulphate environments (solutions of sulphuric acid and ammonium sulphate) was studied in our previous works (Jauberthie and Rendell, 2003). The reaction between some ammonium salts and concrete has been recognised as potentially aggressive since several years: ammonium chloride, sulphate and carbonate being considered the most harmful, whereas ammonium carbonate, oxalate and fluoride being harmless (Biczok, 1972). The effect of pH cementitious mixtures is considered as an important factor in the study of the aggressiveness of sulphate (Cao et al., 1997).

The introduction of granulated blast furnace slag (BFS) can consume much of Portlandite provided by the Portland cement (PC) during hydration. It reduces the pH of the mixture and therefore improves the resistance in acids aggressive environments (Achoura et al., 2008). So we have shown that the increase of the specific surface (3500 cm^2/g to 4200 cm^2/g) clearly improves the mechanical resistances for the concrete containing up to 30% of slag (comparable resistances to those of concrete without slag) (Naceri and Messaoudene, 2006).

The use of marble powder as a cement replacement has recently been the object of several research projects. Agarwal and Gulati (2006) showed that the presence of marble powder in the cement matrix improves the early age compressive strength. Topçu et al. (2009) and Alyamac and Ince (2009) showed that four different marble dusts produced in Turkey characterized by a Blaine fineness in the range 3900–5100 (cm^2/g) could be successfully and economically utilized as filler in self-compacting concrete. According to other authors, the incorporation of 8% marble powder resulted in a reduction of mortar strengths (Kavas and Olgun, 2008). In contrast, Valeria et al. (2010) showed that 10% substitution of sand by the marble powder in the presence of a superplasticizing admixture provided maximum compressive strength at the same workability level, comparable to that of the reference mixture after 28 days of curing. Moreover, an even more positive effect of marble powder is evident at early ages, due to its filler ability.

To reduce energy consumption and CO_2 emissions and increase production, cement manufacturers use mineral additives such as slag, pozzolana and limestone (Kenai et al., 2004). Menéndez et al. (2003) showed that the combination of limestone filler (LF) and blast-furnace slag is complementary: the limestone filler improves the early strength of cement while the BFS improves the later strength by the cementing reaction that refines the pore systems. It is proved that the ternary blend of LF, BFS and PC present an optimum strength, better than LF or BFS cement and plain Portland cement (Carrasco et al., 2005).

It is within this context that experimental studies have been carried out on the durability properties of a binary and ternary binder, derived from the partial replacement of Portland cement with slag and marble fillers; samples of normal mortar were exposed for 12 months to two sulphate environments: ammonium sulphate and sulphuric acid at two concentrations (0.05 and 0.25 mol/L)

2 Experimental programs

2.1 Preparation of the binder mixes

Three binders were prepared with a 30% slag and marble fillers cement replacement (table 1). The materials are from Algeria: clinker and gypsum from cement factory of Setif, granulated slag from El-Hadjar steelworks and marble dust from an industrial unit in Bordj Bou Arreridj. The slag was previously studied by Achoura (2005) as sand and as filler. This slag is amorphous (vitrified). X-ray diffraction analysis of marble powder highlights that it is composed only of calcite (100% $CaCO_3$), which explains its color and appearance: white. This marble is a poly crystalline material with well formed crystals tangled up one in another as shown in SEM observation.

Those materials have been crushed to a particle size less than 1mm before being thoroughly mixed, then quartered and prepared in the proportions given in Table 1. A blend containing 65% clinker, 5% gypsum and 30% slag (noted BC), is the reference cement whith known properties (Naceri and Messaoudene, 2006). In TC1 and TC2 mixtures, the slag is partially substituted by 5% and 10% marble powder. Regarding the NF EN 197-1 standard, the binary cement (BC) is similar to a CEMII/B-S and the ternary cement (TC) is similar to CEMII/B-M.

The grinding of the three types of cements was performed using vibratory mills. Granulometric analysis data given by a laser particle-measurement instrument were collected with CILAS 2 equipment. The granulometry of the binders are practically the same for all types of cement. It is lower than 70µm, with a maximum frequency around 11µm.

Table 1. Composition of binder mixes (% by weight).

Mix	Clinker	Gypsum	Slag	Marble powder		NF EN197-1
BC	65	5	30	0	Binary cement	CEM II/B-S
TC1	65	5	25	5	Ternary cement	CEM II/B-M(S, L)
TC2	65	5	20	10	Ternary cement	CEM II/B-M(S, L)

2.2 Preparation of samples

Three types of mortars were investigated in this study: mortar1 containing BC cement, mortar2 containing TC1 cement and mortar3 containing TC2 cement. Mortar samples, 4x4x16 cm^3, were produced in accordance with the standard EN 196-1 (normal mortar: standard sand, water/binder = 0.5 and cement/sand = 1/3). The samples are demoulded after 24 hours and cured in water (20°C) for 28 days. Then, they are kept in the air-conditioned chamber at 20°C, 55% RH until their mass was stabilised.

2.3 Exposure tests

Five regimes of exposure of 1 year duration were used:
- Samples exposed to water.
- Samples exposed to sulphuric acid at low concentration (sulphate concentration 0.05 mol/L)
- Samples exposed to sulphuric acid at high concentration (sulphate concentration 0.25 mol/L)
- Samples exposed to ammonium sulphate at low concentration (sulphate concentration 0.05 mol/L)
- Samples exposed to ammonium sulphate at high concentration (sulphate concentration 0.25 mol/L)

The choice of ammonium sulphate and sulphuric acid is dictated by their high aggressiveness on the concrete. On the one hand, the ammonium sulphate is commonly used as fertilizer to acidify alkaline soils. It is probably the most aggressive sulphate vis-à-vis Portland cement (Biczok, 1972). On the other hand, the aggressiveness of sulphuric acid is due to two phenomena: its acidity and the formation of expansive products (gypsum and ettringite). In sewage systems, concrete pipes damage is mostly attributed to corrosion by biogenous sulphuric acid (Kaempfer and Berndt, 1999). The exposure period (12 months) is very important to study the durability of cements containing slag and marble fillers.

3 Results

3.1 Visuals observations

Fig. 1 shows the samples after 1 year of exposure to the sulphate solutions. The following observations can be drawn:
- In the bath [$(NH_4)_2SO_4$ (0.05 mol/L)], the sample surface was not altered. In contrast, in the bath [$(NH_4)_2SO_4$ (0.25 mol/L)], cracks can be observed at the surface. Also, all samples exhibited a layer of fibres (invisible to the naked eye) that resembles a needle-like surface covering.
- In the bath [H_2SO_4 (0.05 mol/L)], sample surface is slightly corroded. In the highest concentration of acid (0.25 mol/L), sample surface is heavily degraded with dislodged grains of quartz. A dense layer of gypsum was formed. Further X-ray analysis confirms the chemical composition of this layer.

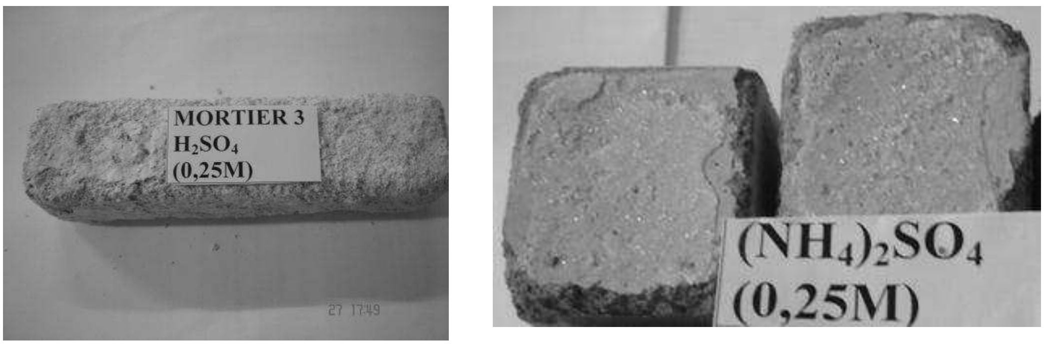

Figure 1. Visual observations.

3.2 Mechanical characterization

Fig. 2 shows the 1 year flexural strengths obtained for the different types of mortars. For each regime of exposure, two samples were tested under 4-point bending. For the specimens exposed to sulphuric acid (0.25 mol/L), a piece of cardboard is placed on both sides of support to enable proper application of the load and better characterization of the mortar intrinsic strength.

A global observation leads to the following remark: the flexural strength of samples slightly decreases with increasing the concentration of sulphate. At high concentration (0.25 mol/L), the reduction in strength is remarkable for all mortars. The exposure to ammonium sulphate systematically conducts to the higher loss of flexural strength. The reference mortar 1 (with 30% of slag) with a minimal strength of 6MPa (85% of its original H_20 strength) seems to be the more resistant to sulphate attack. Mortar 3 (with 10% of marble) presents the lowest resistance.

Fig. 3 shows the 1 year compressive strength. The values are an average of four compressive test results.
After exposure in low concentrated sulphate solution (0.05 mol/L), the strengths of all mortars are 10% to 20% higher than those of samples stored in water. In contrast, the samples exposed to high concentrated (0.25mol/L) sulphate solution, the strengths significantly decrease (a drop of about 50%). Unlike previous observations for flexural strength, sulphuric acid is more damaging to compressive strength than ammonium sulphate.

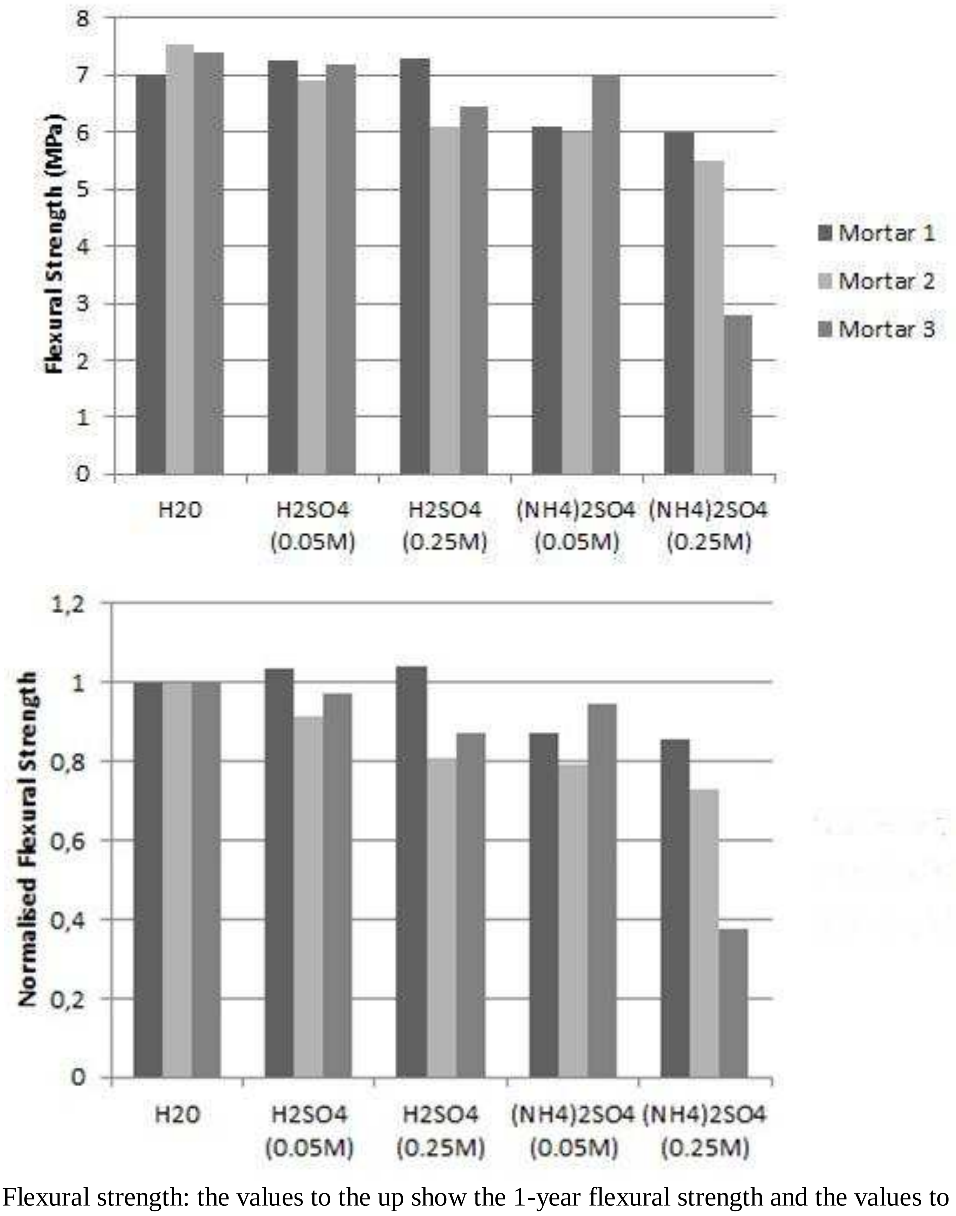

Figure 2. Flexural strength: the values to the up show the 1-year flexural strength and the values to the bottom are normalized to the strength after 1-year exposure in H_2O bath.

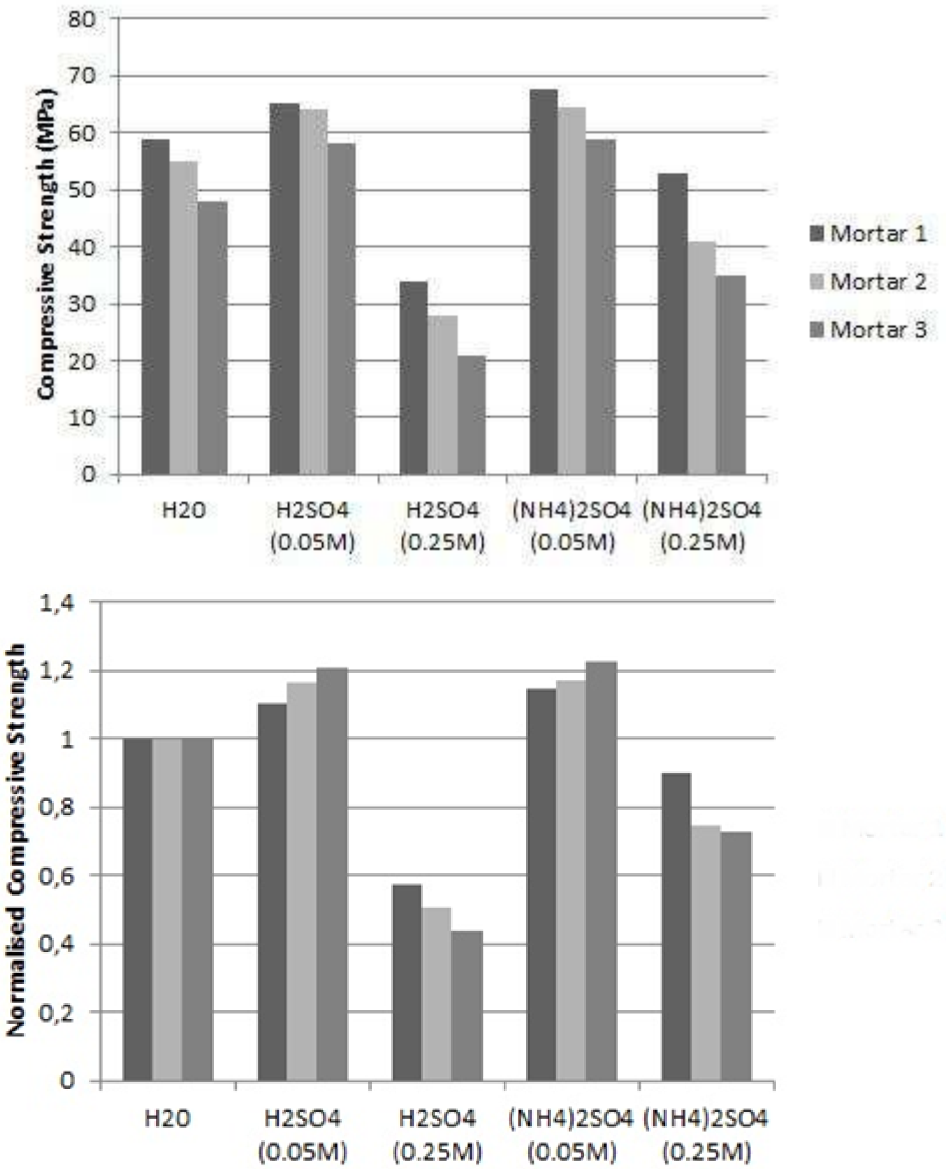

Figure 3. Compressive strength: the values to the up show the 1-year compressive strength and the values to the bottom are normalized to the strength after 1-year exposure in H_2O bath.

3.3 Depth of reduced alkalinity

The test for reduction in pH of concrete (phenolphthalein test) consists of spraying a freshly fractured surface of concrete with phenolphthalein solution, which turns pink when the pH is above 12, which is close to the pH of new concrete. One can consider the sections of coloured concrete to be sound, whereas those with no colour are considered to be depassivated. Examples can be seen in Fig. 4.

Samples stored in the low concentrated ammonium sulphate bath (0.05mol/L) show an area of reduced alkalinity. These area have an estimated thickness of 1mm.There is virtually no damage to samples stored in low concentrated sulphuric acid. In high concentrated sulphuric acid (0.25 mol/L), damage is more important and area of reduced alkalinity have an estimated thickness of 1mm. Finally, in high concentrated ammonium sulphate, the area of reduced alkalinity is significantly greater with a thickness of 2 to 4 mm. Results are resumed in Table 2. Results for high concentrated ammonium sulphate show a good correlation between the marble filler content and the thickness of the area of reduced alkalinity. The depth of reduced alkalinity increases with the amount of marble.

Table 2. Depth of reduced alkalinity (mm).

Mortar type	H_2O	H_2SO_4 (0.05M)	H_2SO_4 (0.25M)	$(NH_4)_2SO_4$ (0.05M)	$(NH_4)_2SO_4$ (0.25M)
1	0	0	1	1	2
2	0	0	1	1	3
3	0	0	1	1	4

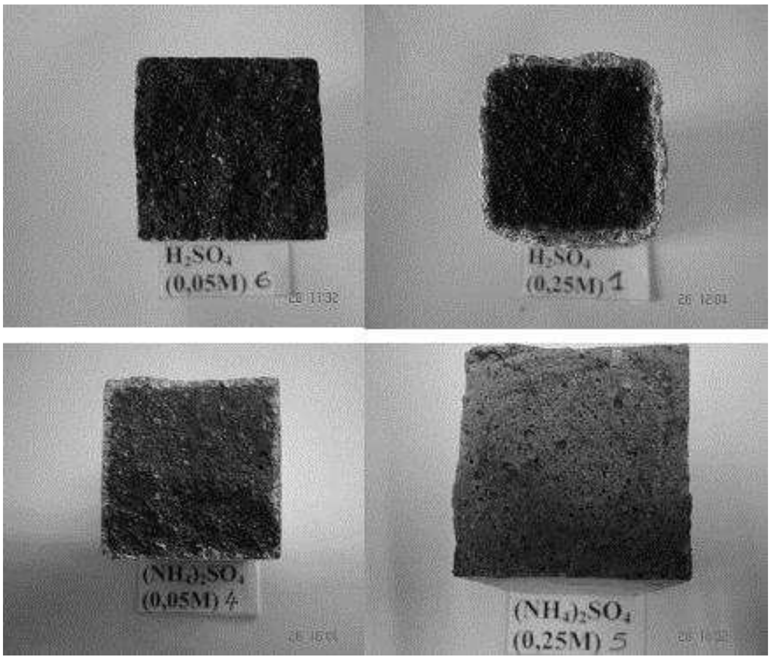

Figure 4. Depth of reduced alkalinity of the mortar indicated by the phenolphthalein solution.

3.4 X-ray diffraction of the surface

X-ray diffraction analysis was carried out on the surface of the mortar that has been in contact with the sulphate solution (0,25mol/L). The deposits formed on the surface of the mortar samples were carefully removed by scraping, care being taken not to remove any of the mortar matrixes. These deposits were ground to a powder and analysed by XRD. For a concentration of 0,05mol/L, it was difficult to scratch, the surface was not altered. The samples subjected to sulphuric acid attack were heavily degraded with dislodged grains of quartz. Between the quartz grains, the surface was covered with a dense white deposit. The diffraction analysis (fig. 5) confirmed the presence of quartz surrounded by gypsum. In contrast, the surface of the sample exposed to ammonium sulphate was less degraded, with a light surface deposit of transparent needle-like crystals growing from the surface. Analysis showed a smaller quantity of quartz and gypsum present than was found in the case of acid attack. The rest of the surface consisted of calcite, as indicated by peaks on the diffraction diagram.

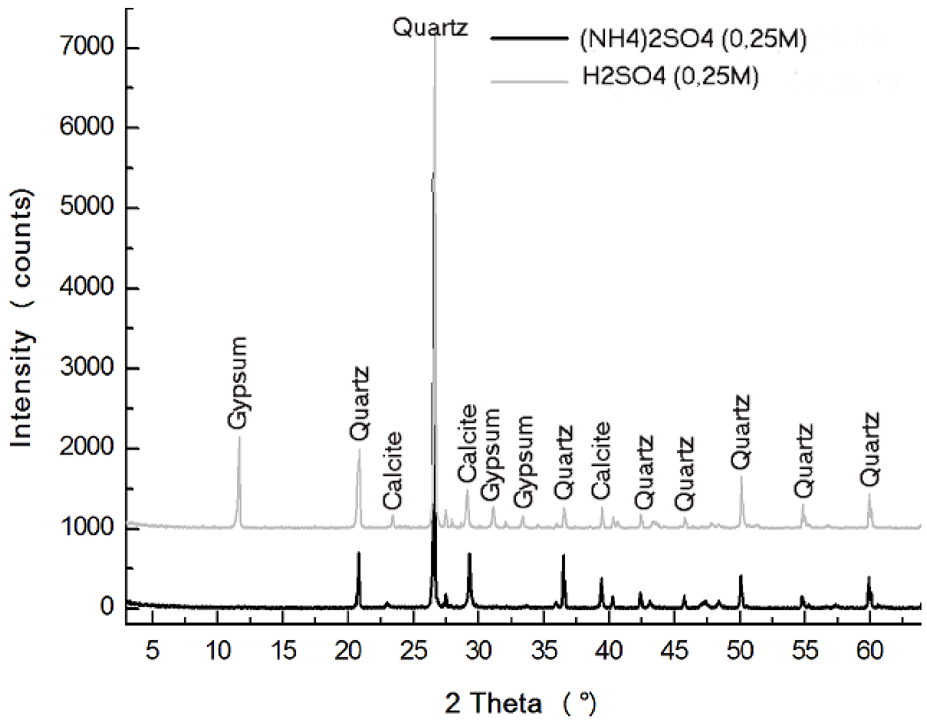

Figure 5. *XRD* pattern of surface deposits on mortar in sulphate solution (Cu Kα radiation, Ni filtred).

3.5 Scanning electron microscope analysis

The external surfaces of the samples subjected to sulphate environments were examined by using the scanning electron microscope and the micro-probe.

The sample exposed to high ammonium sulphate concentration (0.25mol/L) exhibited a surface layer of fibres transparent to the naked eye that resembled a needle-like surface covering). The length of these crystals was often of the order of millimetres and their section, of the order of tens microns, was hexagonal. Micro-probe analysis confirmed that these crystals were gypsum (the most significant peaks being sulphur, calcium and oxygen) (fig.6).

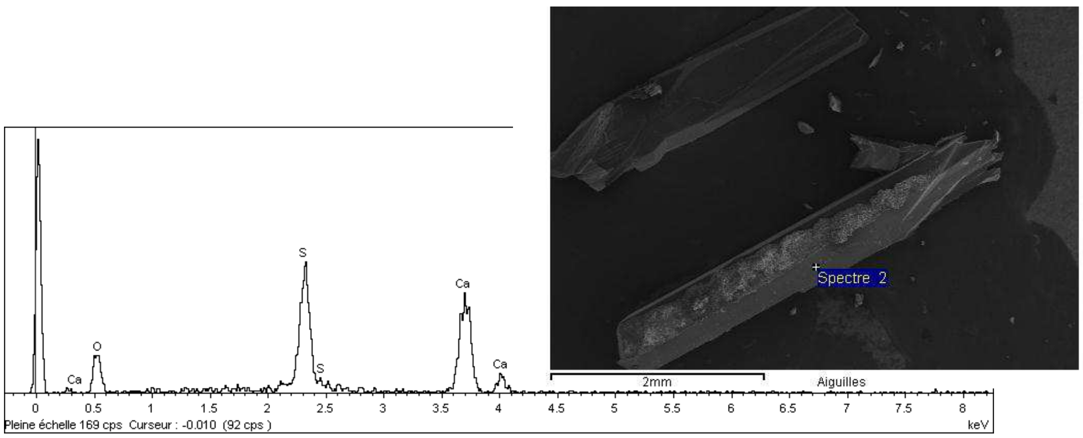

Figure 6. Observation and micro-probe analysis of fibres on the surface attacked by ammonium sulphate (0,25mol/L).

Fig. 7 show significant quantity of sulphur in the interior exterior of the surface of the mortar 3 sample (of the order of 3mm from the surface). The rest of the field is composed of hydrates of calcium silicate.

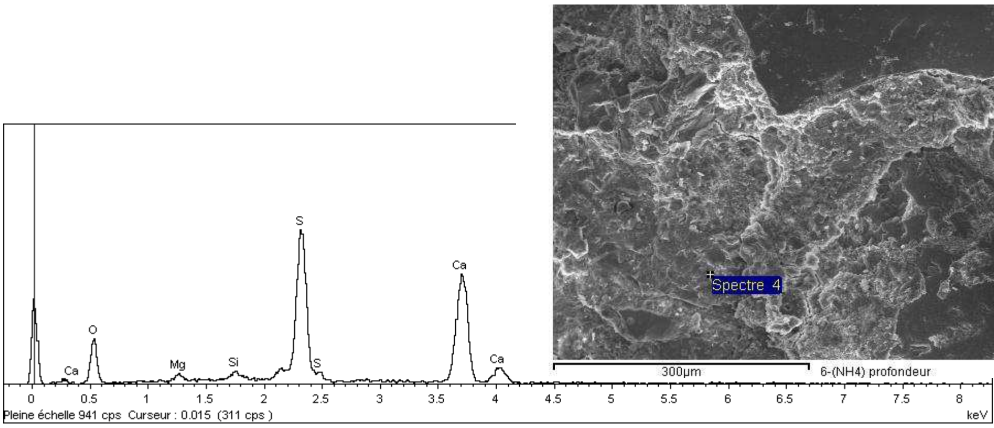

Figure 7. Micro-probe analysis of the interior of the surface of mortar 3 attacked by ammonium sulphate (0,25mol/L) - 3mm from the surface.

At a depth larger than 3mm, the overall chemical analysis (Fig. 8) shows the formation of a large quantity of gypsum, probably due to the reaction of the sulphate solution with portlandite. The rest of hydrates are composed of silicates (presence of Ca and Si) and probably ettringite (presence of Al).

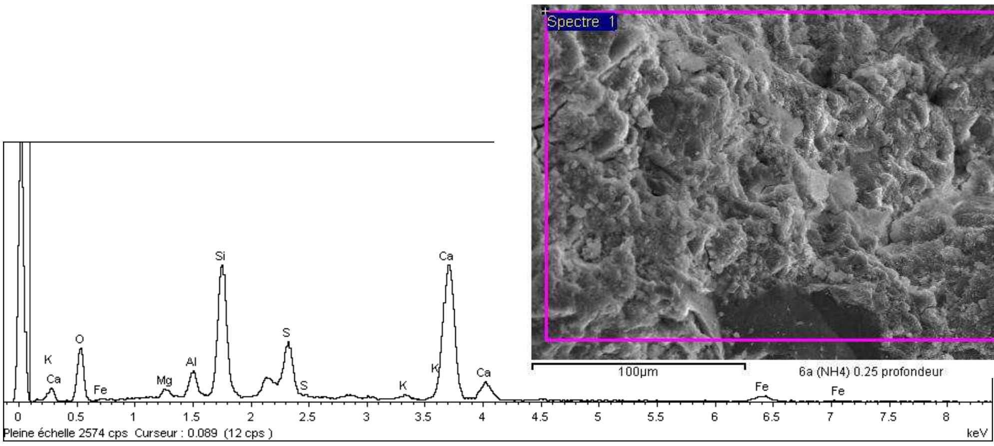

Figure 8. Micro-probe analysis in the interior of mortar 3 attacked by ammonium sulphate (0,25mol/L) - 4mm from the surface.

For the samples exposed to a lower concentration of ammonium sulphate (0.05mol/L), the quantity of sulphur was greatly reduced at a depth of more than 1 mm.

The surface that was exposed to high concentration of sulphuric acid (0,25 mol/L) had a nature that was quite different. In spite of the different appearance of this layer, it was identified, by microanalysis, as gypsum. The microanalysis carried out on the surface of the samples showed that there was development of surface formation, not of the same form as found in the previous case. Nevertheless, it was identified as gypsum. At a depth of the order of 2mm, the quantity of sulphur was significant (fig.9). In contrast, samples subjected to low concentration (0.05 mol/L), the quantity of sulphur was totally absent at 1 mm.

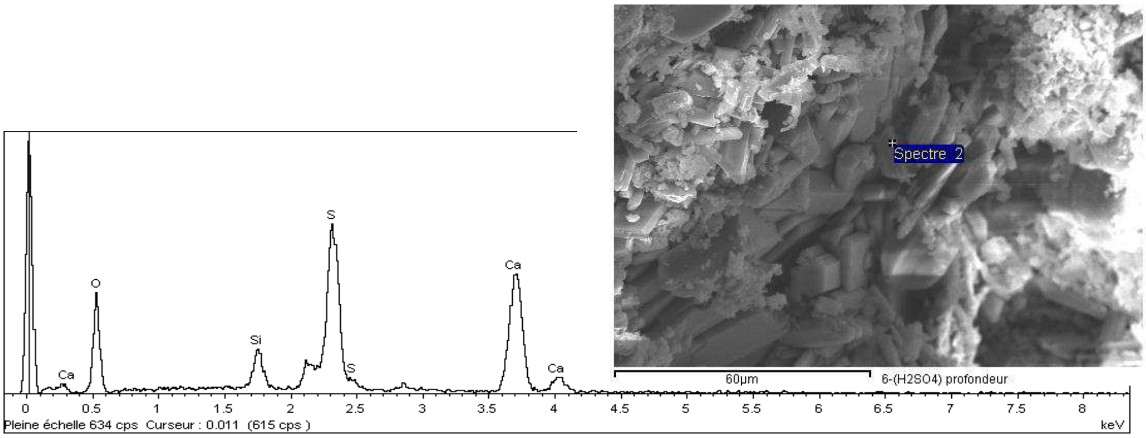

Figure 9. Micro-probe analysis of the interior of the surface of mortar 3 attacked by sulphuric (0,25mol/L).

4 Conclusions

Exposure of samples for duration of 12 months confirms that the durability of concrete is strongly related to the type of cement used, type of cation linked to sulphate and finally, the concentration of sulfates.

For a concentration of 0.25 mol/L of sulphate solution, the following conclusions can be drawn:

- Mortars exposed to sulphuric acid develop a dense surface gypsum deposit, whereas, those mortars exposed to ammonium sulphate develop a sparse surface layer of needle-like crystals identified as gypsum.
- The mechanism of attack in the case of mortar exposed to sulphuric acid is principally a surface phenomenon, the expansive action of the gypsum acting to dislocate aggregate and to increase microcracking at the surface. The attack of surface causes a decrease in sample section. On the other hand, dislodged grains of quartz will cause a puncture in sample: These two phenomena contribute to a significant decrease in compressive strength. The resistance of samples exposed to ammonium sulphate (0.25 mol/L) slightly decreases. It varies between 35 and 53Mpa, especially for mortar containing cement with 10% marble powder, this can be explained by the calcite dissolution in the presence of strong acid such as sulphuric acid.
- In ammonium sulphate (0.25mol/L), the surface deposit of gypsum is sparse and the damage to the concrete occurs to a greater depth (4mm). The lack of sulphur found in the surface zone indicates that the mechanism of deterioration is due to the dissolution of Ca^{2+} resulting from the reaction of portlandite with sulphate. But despite this, the resistance varies between 35 and 53MPa, this confirms the pozzolanic effect of granulated slag and its latent hydration. The first hydrates will be those of the clinker, C-S-H and $Ca(OH)_2$. Next, the excess of lime activates the hydration of grains slag with CSH texture similar to those of CEMI. This confirms XRD analysis which showed a reduced quantity of portlandite.

For a concentration of 0.05mol/L, the SEM and microanalysis results show that the presence of sulphur is virtually non-existent in the matrix of mortars exposed to sulphuric acid, whereas, it is negligible for those mortars exposed to ammonium sulphate. Moreover, the compressive strengths were unchanged, high performance is recorded. In ammonium sulphate, there was a slight decrease in tensile strength due to the surface which was slightly cracked.

To reach a better durability in sulphate environments at concentrations above 0.05mol/L, the quantity of marble filler will be limited to 5% and the slag filler between 25 and 30%. To maximize durability, the portlandite released during cement hydration must be fully consumed by the pozzolanic effect: the slag must be adequate and sufficient time due to slow reaction kinetics. On the other hand, the marble filler plays an important role on the compactness, but its dosage should be limited between 5 and 10%.

The addition amount should therefore be limited to 30% to avoid alteration durability characteristics.

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